Opening the analytical black box: Insights into interferences, corrections, and data quality

Dr. Anthony J. Bednar

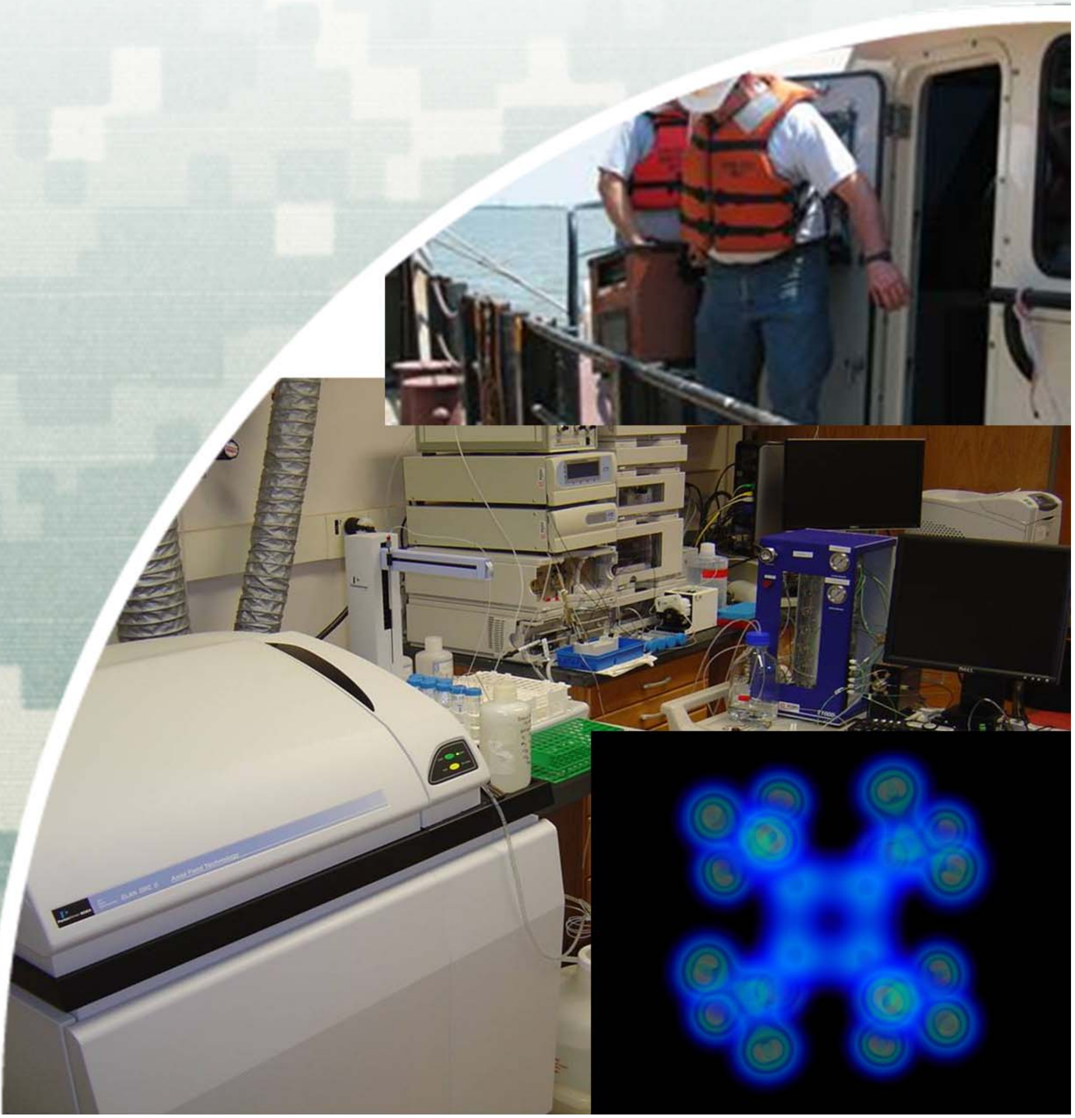
Research Chemist

USACE ERDC-EL

29 March 2012

D.M. Sirkis, W.E. Harris, T.J. Kelly

USACE-NAP



US Army Corps of Engineers
BUILDING STRONG®

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **29 MAR 2012**	2. REPORT TYPE	3. DATES COVERED **00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE **Opening the analytical black box: Insights into interferences, corrections, and data quality**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Engineer Research and Development Center,Environmental Laboratory,Waterways Experiment Station, 3909 Halls Ferry Road,Vicksburg,MS,39180-6199**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

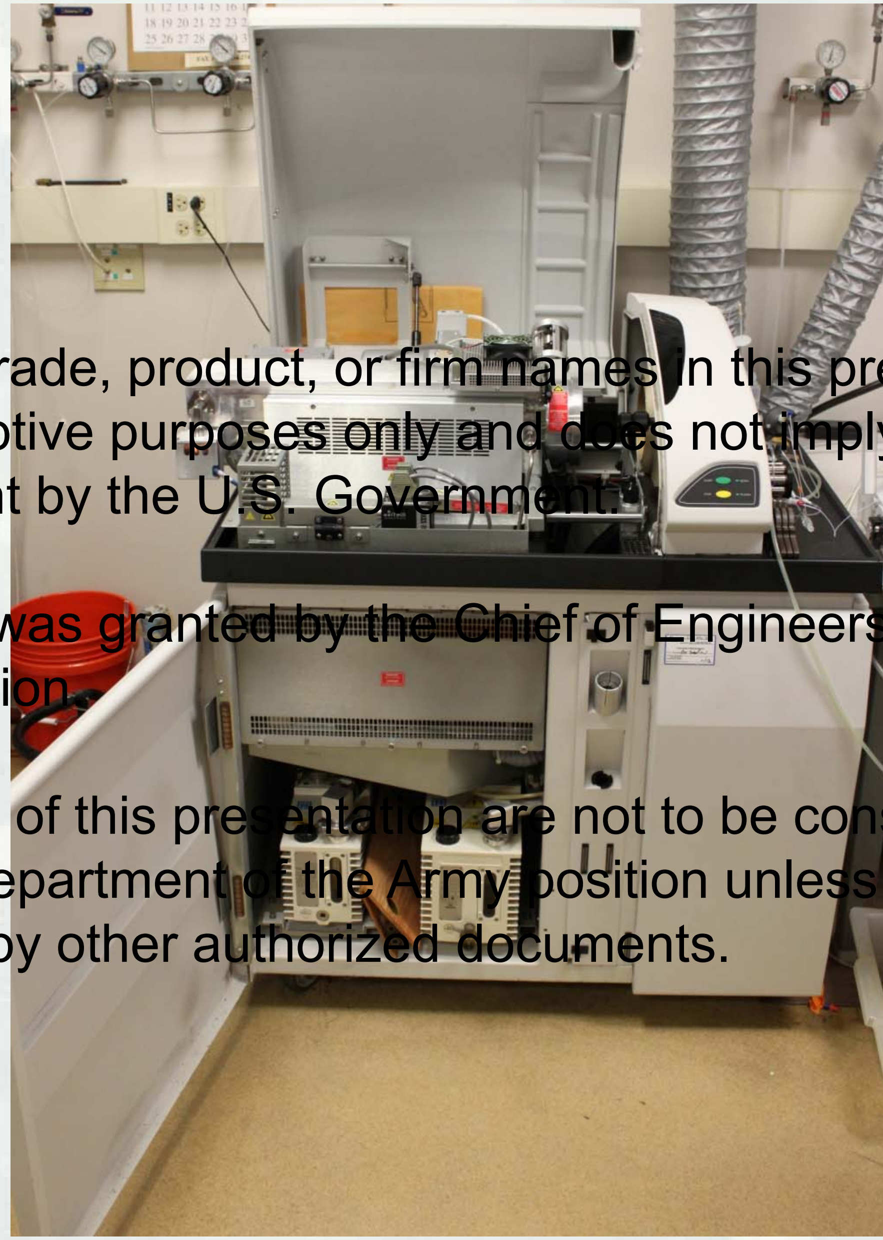
13. SUPPLEMENTARY NOTES
Presented at the 9th Annual DoD Environmental Monitoring and Data Quality (EDMQ) Workshop Held 26-29 March 2012 in La Jolla, CA.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**16**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18



The use of trade, product, or firm names in this presentation is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Permission was granted by the Chief of Engineers to publish this information.

The findings of this presentation are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Overview

- Interferences in various techniques
  - GF-AAS
  - ICP-AES
  - ICP-MS
- Interference corrections
  - Spectroscopic overlaps
    - IEC
    - MSF
  - Correction equations
  - Collision and Reaction Cell Technology
- Pitfalls of 'black box' analysis
  - Rule of thumb
    - Ignore Rules of Thumb

Techniques and Issues

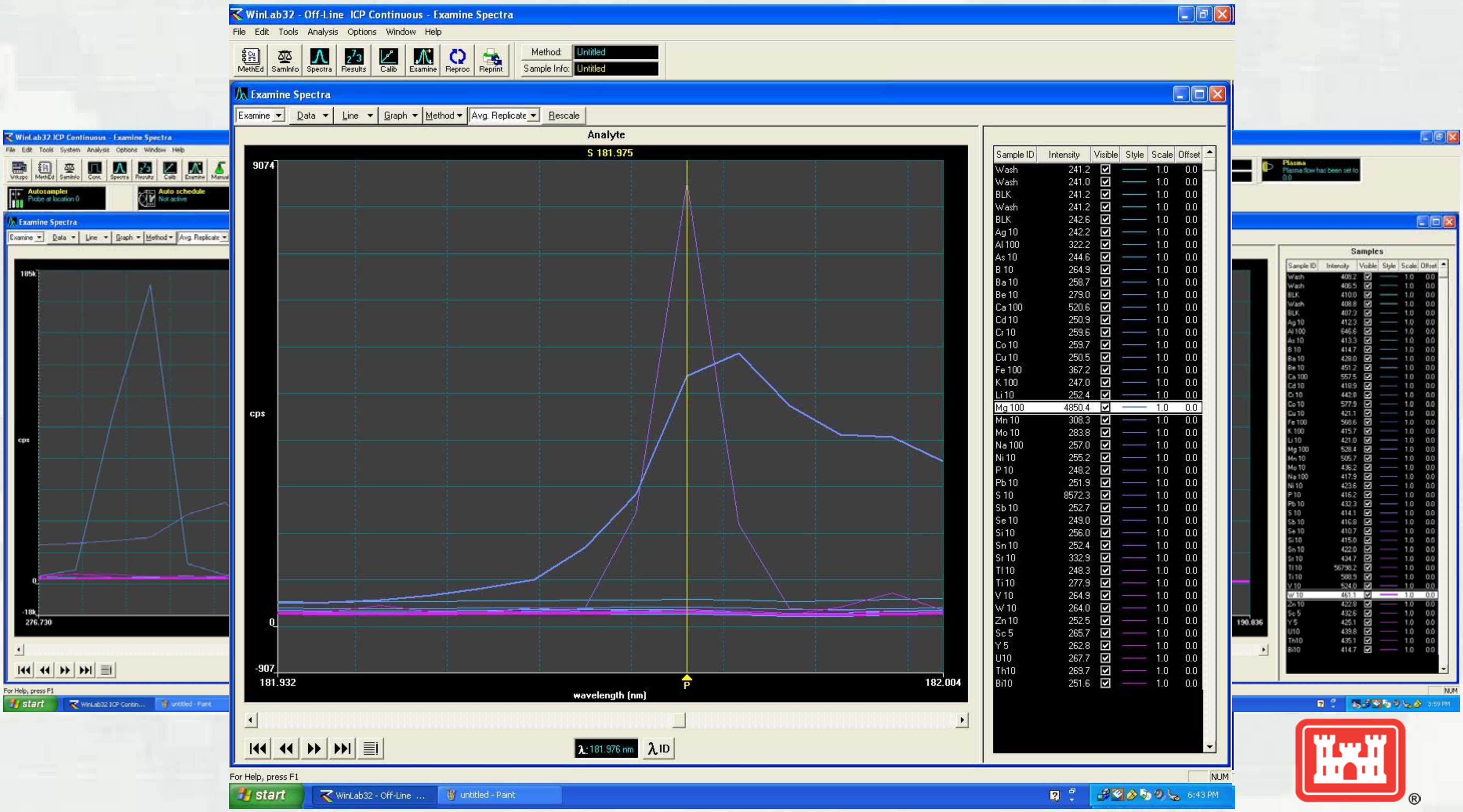
- GF-AAS
  - ► Major interferences
    - • Atomization suppression
    - • Volatilization
    - • Molecular and Atomic absorptions
  - ► Corrections
    - • Optimization of thermal pretreatment and atomization
      - ▷ Hotter if suppressed
      - ▷ Cooler if volatilization
    - • 'Correct' matrix modifier
      - ▷ 'Universal' matrix modifier (Pd-Mg) vs historical modifiers (Ni, Phosphate, etc.)
    - • Zeeman and deuterium background corrections

Techniques and Issues

- ICP-AES
  - Major interferences
    - Nebulization suppression or enhancement
    - ‘Plasma loading’
    - Spectroscopic overlaps
  - Corrections
    - Internal standards
      - Generally correct for nebulization and plasma issues
      - Can yield spectroscopic interferences
    - Interelement correction factors (IEC)
      - Mathematical formula: 10 mg/L of element X yields 0.1 mg/L false element Y
      - Usually best for direct spectral overlap
    - Multicomponent Spectral Fitting (MSF)
      - Mathematical modeling of spectra shape
      - Generally better for complex or variable interferences

ICP-AE Spectra

- Spectral overlaps in ICP-AES



Techniques and Issues

- ICP-MS
  - ▸ Major interferences
    - Some are identical to ICP-AES
      - ▷ Nebulization suppression or enhancement
      - ▷ ‘Plasma loading’
    - Isobaric interferences
      - ▷ Isotopic overlap
      - ▷ Molecular/polyatomic species
      - ▷ Double charged ions

Techniques and Issues

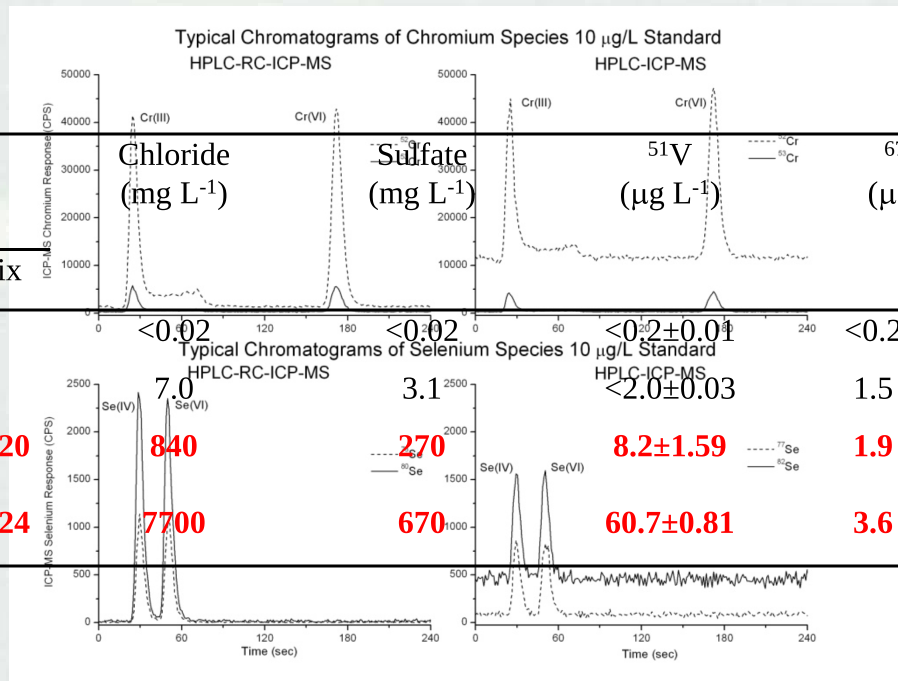
- ICP-MS
  - Corrections
    - Internal standards
      - Generally correct for nebulization and plasma issues
      - Can yield isobaric interferences (e.g. formation of oxides)
    - Mathematical correction equations for isotopes or molecular species
      - Relatively straight forward for isotopes (measure another isotope and subtract based on isotopic abundance
      - Molecular interferences are slightly more complex
      - Assumes correction isotopes are clean
    - Collision Cell
      - He or other inert gas used to ‘break up’ or ‘slow down’ molecular and polyatomic species
      - Ineffective with double charged species
    - Reaction Cell
      - Reactive gas used to ‘break up’ polyatomics or make specific polyatomics
      - E.g. ^{75}As analyzed as ^{91}AsO or ^{51}V analyzed as ^{67}VO

Correction Equations

- Example: $^{40}Ar^{35}Cl$ on ^{75}As
  - Ignores other species, e.g. $^{38}Ar^{37}Cl$
  - ^{75}As = m/z 75 – 3.127 (m/z 77 – 0.874 m/z 82)
    - 3.127 is 35:37 isotope ratio
    - m/z 77 measures $^{40}Ar^{37}Cl$ + ^{77}Se
    - m/z 82 measures Se in sample to remove Se component in 77 m/z term using 77:82 ratio of 0.874.
    - Similar correction is used for $^{16}O^{35}Cl$ on ^{51}V using ^{52}Cr and ^{53}Cr
  - Correction equation depends on correction isotopes being clean of 'extraneous' interferences (e.g. ones other than the Ar-Cl species of interest
    - Even though this is a commonly used equation, it fails this important test, ^{82}Se is far from 'clean'
    - $^{34}S^{16}O_3$ and $^{1}H^{81}Br$

Collision and Reaction Cell Technology

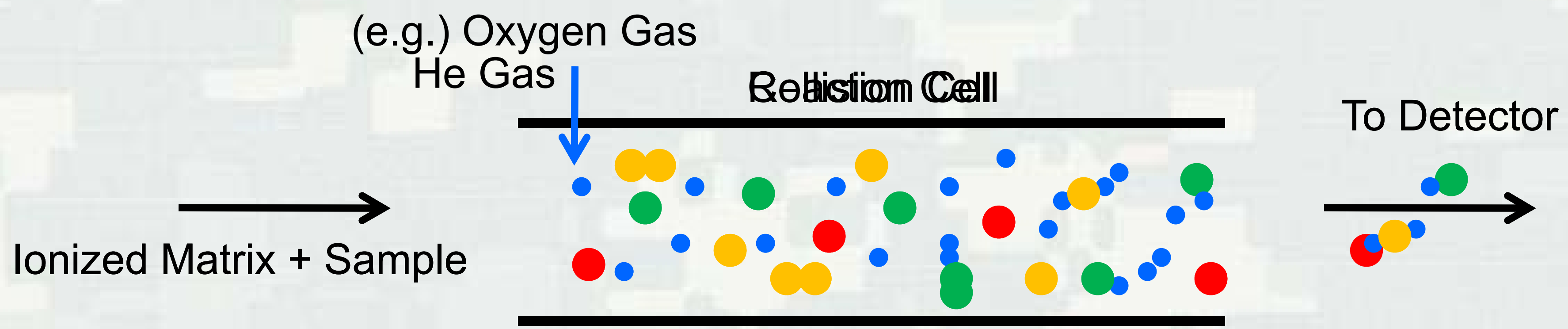
- Examples
  - ► ^{52}Cr, ^{53}Cr, ^{67}VO
    - Oxygen reaction gas removes Ar-C dimers (m/z 52 and 53)
    - OCl dimers, however, are not, thus the need for creation of VO
      - ▷ Similar application for AsO



Analyte Measured / Sample Matrix	Chloride (mg L^{-1})	Sulfate (mg L^{-1})	^{51}V (µg L^{-1})	^{67}VO (µg L^{-1})	^{67}VO-Zn corrected (µg L^{-1})
DI Water	<0.02	<0.02	<0.2±0.01	<0.2 ± 0.00	<0.2 ± 0.02
Tap Water	7.0	3.1	<2.0±0.03	1.5 ± 0.12	1.1 ± 0.04
River Water 20	**840**	**270**	**8.2±1.59**	**1.9 ± 0.67**	**1.1 ± 0.18**
River Water 24	**7700**	**670**	**60.7±0.81**	**3.6 ± 0.06**	**1.8 ± 0.03**

Collision and Reaction Cell Technology

- Examples when it may not work
  - Double charged ions
  - Rare Earth Elements ($^{149\ \&\ 150}$Sm, ^{150}Nd, and ^{151}Eu) on ^{75}As
  - Collision Cell ineffective because double charges and analyte ions have the same cross sectional area
    - Not removed via dissociation or kinetic energy discrimination



Rare Earth Interferences

- Second ionization potential sufficiently low to allow double charges
- Rarely
- al facility detecte
- GF-AAS
  - Con
- Reactio
  - Eith n oxid

Lab ID	ICP-MS As ug/L	ICP-MS %REC	RC-ICP-MS As ug/L	RC-ICP-MS %REC	GF-AAS As ug/L	GF-AAS %REC
1021401-01	**8.5**		**2.2**		**0**	
1021401-01 Dup	7.9		2.1		0.1	
1021401-01 Spike	53.2	111.75	44.5	105.75	18.4	92
1021401-02	**4.7**		**5.3**		**<4**	
1021401-03	**3.5**		**3.2**		**2.4**	
1021401-04	**1.2**		**1.1**		**0.8**	
PBS	<0.5		<0.5		<1	
CRA	0.51	102	0.52	104	1	100
LCS	25.8	103.2	26.1	104.4	25.3	101.2
ERA	167	99.40476	171	101.7857	198	117.8571
CCV	50.7	101.4	53.6	107.2	50	100
CCB	<0.5		<0.5		<1	

Repeat Issue

- Water district new aquifer samples
  - Post-treatment water containing suspended sediment

Analyte	Mass	CPS	ug/L	CPS in blank
Y	89	1296811		846987
Sc	45	334897		298284
V	51	234243.8	127.8	
V-1	51	234034.4	129.4	
Cr	52	133706.6	76.0	
Cr	53	15175.82	74.8	
As	75	15752.88	52.6	
As-1	75	16656.18	50.0	
Se	77	352.674	9.4	
Se	82	734.032	9.1	
Mo	95	3249.3	5.0	
Mo	97	1976.235	4.9	
Rh	103	629007.4		626031

GFAAS confirmation of As concentration 29 µg/L

Analyte	Mass	ug/L
Ce	140	1964.8
Dy	163	86.4
Er	166	38.4
Eu	153	38.1
Ho	165	15.2
La	139	903.5
Lu	175	4.0
Nd	146	754.8
Pr	141	209.2
Sm	147	137.8
Tb	159	18.5
Sc	45	46.7
Tm	169	4.9
Yb	172	27.6
Y	89	376.9
In	115	
Gd	157	134.5
Rh	103	

Analytical Suggestions

- Add more internal standards
  - ^{89}Y is not particularly good for many elements as internal standard (based on ionization potential for its mass range), but it is good for determining matrix interferences and potentially oxides (e.g. ^{105}YO)
  - Use 'different' internal standards and compare to traditional internal standards
    - ^{103}Rh generally works as well as ^{72}Ge as an arsenic internal standard but is not as susceptible to interferences
- Monitor multiple isotopes (or wavelengths in ICP-AES)
  - Method 6020 and 6010 'guidance', use multiple data points when available
  - For mono-isotopic elements, monitor with and without correction equations
- Monitor for known or expected interferences
  - ^{52}Cr and ^{53}Cr or ^{77}Se and ^{82}Se, even if not analytes of interest, will tell you important information about potential matrix issues
- Use the 'correct' analytical technique
  - For the analyte and reporting range of interest

Conclusions

- GF-AAS is an old technique, but nevertheless useful and an important tool in the toolbox
- Using standard ICP-AES emission wavelengths and known IEC is usually fine, but certain interferences require alternative correction methods, such as MSF
- ICP-MS is has interferences that can't be corrected mathematically
- Using standard isotopes and correction equations is generally fine, but at least monitor other isotopes and monitor with and without correction equations
- Collision or Reaction Cell ICP-MS does not takes care of all other interferences in ICP-MS, but is a powerful tool if understood and used properly

Questions

Thanks!